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# Combined particle mass spectrometer – Quartz crystal microbalance apparatus for *in situ* nanoparticle monitoring during flame assisted synthesis

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#### ABSTRACT

A newly developed apparatus for simultaneous *in situ* monitoring of size, mass and number concentration of a flame synthesised particle aerosol is presented. The diagnostics methodology is relying on combination of particle mass spectrometry and quartz crystal microbalance techniques. The analysis protocol includes molecular beam sampling, sorting the charged particles constituent according to mass/charge ratio (*m*/*ze*) via electrostatic deflection, and detection of the neutral particles by monitoring the variation of the quartz crystal oscillation frequency upon exposure to the particle – laden molecular beam. From these measurements, the total mass concentration and probability density distribution of *m*/*ze* could be directly determined, allowing to deduce the particle number concentration in the aerosol, at least in relative units. The feasibility of the method was demonstrated on the example of iron oxide nanoparticles (NPs) forming in  $CH_4/O_2/N_2$  dual stage flame doped with iron pentacarbonyl, Fe (CO)<sub>5</sub> as a precursor of iron oxide NPs. Sensitivities of  $6 \times 10^4$  NP/s and  $8 \times 10^6$  NP/s were achieved for charged and neutral particles, respectively. Possible implications of the obtained results on the elucidation of iron oxide NP formation mechanism are discussed.

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#### 1. Introduction

Synthesis of metal oxide nanoparticles (NP) in flames offers several important advantages, including control over particle size and morphology and a route to large-scale production of nanomaterials [1]. Hence, it is not surprising that gas phase combustion is routinely used for production of variety of nanosculpted metal oxides. The metal oxide nanomaterials are used as pigments, opacities, flowing aids, for optical fibers, telecommunication and as highly efficient heterogeneous catalysts. Among various metal oxides, iron oxide NPs monitored in this work are used in diverse applications, including optical magnetic recording, catalysis, gas sensors, targeted drug delivery, magnetic resonance imaging, and hyperthermic malignant cell therapy (see for instance review by Lu et al. [2] and references therein). The functionalities of iron oxide NPs in various applications can be highly dependent on their characteristics, such as size, morphology and oxidation state. These characteristics depend on flame conditions (e.g., fuel/oxidizer ratio, temperature), choice of a flame fuel, particle precursor, and the position where the particles are collected [3-8]. Hence, using a flame

\* Corresponding author. E-mail addresses: cheskis@post.tau.ac.il, scheskis@me.com (S. Cheskis). source allowing for a wide range of operating conditions – is of paramount importance for acquiring the ability to tune the properties of synthesized NPs. The flame source used in this work is a hybrid McKenna burner, where the primary flame supported on the porous sinter provides the energy necessary to support the central flame containing the NP precursor (see Section 2), even when the later has fuel/oxygen ratio which otherwise would not allow stable burning conditions.

Current understanding of the mechanisms governing flame assisted NP synthesis is insufficient to enable full control over particle production. One of the main challenges is the development of methodologies for *in situ* NP monitoring in reactive flows (e.g., flame), since the *ex situ* methods (electron microscopy, X-ray scattering, etc.) are very time consuming and cannot provide in a timely manner sufficient experimental data for experiments with strongly and rapidly changing flame conditions.

Particle Mobility Spectrometer (see for example [9-11]) is very effective for measurement of the particle sizes when their shape is known. Its application for low pressure flames would require further pressure reduction, which can make electrical mobility measurements under viscous gas flow regime more difficult.

A particle mass spectrometer (PMS), employing molecular beam sampling [3,12], was successively applied for *in situ* measurements of the mass distribution of charged NPs forming in flame. Measure-

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#### Nomenclature

A b C <sub>m</sub> d ∆d	working area of the quartz crystal $(m^2)$ distance between the plates of the deflection capacitor (m) mass density sensitivity constant of the quartz crystal $(Hz cm^2/ng)$ distance between the Faraday cup and the <i>x</i> -axis $(m)$ width of the Faraday cup $(m)$	mnanoparticle mass $(ag, ag = 10^{-18} g)$ $\Delta M$ deposition induced mass uptake of the quartz $U$ deflection capacitor voltage (V) $v_x$ nanoparticle velocity component along the x $v_y$ nanoparticle velocity component along the y $z$ particle charge state	-axis (m/s)
e f Δf I l <sub>c</sub> l <sub>g</sub> L	charge of the electron (C) frequency (Hz) decrease in the oscillation frequency of the quartz crys- tal (Hz) force (N) electrical current (A) length of the deflection capacitor plates (m) distance between the velocity measurement chopper plates (m) distance between the deflection capacitor and the PMS- QCM assembly (m)	AcronymsDCPdeflection capacitor plateDFBdistance from the burner (mm)FCFaraday cupIPCiron pentacarbonylNPnanoparticleMFCmass flow controllerPDFprobability density functionPMSparticle mass spectrometerQCMquartz crystal microbalanceVMCPvelocity measurement chopper plate	

ment of total mass distribution by this method is independent of particle shape and can be conducted within several seconds.The charged NPs can be formed in flames by various mechanisms: thermal ionization, chemi-ionization at the NP surface, ion forming chemical reactions followed by charge transfer to NPs, etc. (e.g., [13,14]). The relative contribution of different mechanisms for charged NP formation remains an open question and is highly dependent on flame conditions and composition, making quantitative predictions of ionization efficiency difficult.

Recently, we have demonstrated that the Quartz Crystal Microbalance (QCM) technique allows for spatially-resolved *in situ* mass concentration measurements of flame produced NPs, both charged and uncharged [15]. However, the QCM technique alone cannot reveal the size of the NPs and hence, does not allow to determine their number concentration. On the other hand, the PMS technique does not provide information regarding the total quantity of NPs, since only charged particles are detected. One cannot draw conclusions regarding the total NP amount based on the measurements of charged particles alone. This is due to the fact that the amount of charged NPs depends not only on the total particle amount, but also on the ionization efficiency which may (and does, as will be shown subsequently in this paper) change with local position in the flame.

The combination of QCM and PMS in one apparatus allows to address this problem. Simultaneous measurements of total mass of NPs in the molecular beam by QCM, and particle size distribution along with charged particle current by PMS provide a great deal of new information regarding the NP formation processes. In this work we demonstrate for the first time the advantages of the combined PMS-QCM apparatus on the example of iron oxide NPs formed in methane/oxygen/nitrogen flames doped with iron pentacarbonyl (IPC).

#### 2. Experimental methodology

The experimental setup is schematically depicted in Fig. 1. It consists of a combustion chamber and a combined PMS-QCM apparatus. The combustion chamber houses a modified McKenna flat flame burner which includes a water cooled bronze porous plug with a diameter of 60 mm. On this burner a stoihiometric methane/oxygen/nitrogen flame (hereafter called primary flame) is stabilized. The burner is modified by the incorporation of a narrow central tube (4.2 mm I.D.) used for stabilization of a secondary

flame with various compositions. Thus, the modified burner allows to sustain two flames: a primary one, which is flat with a front located at about 11 mm from the burner under our conditions; and a secondary one, having a bulb shape with curved flame front extending as far as 23 mm from the burner. This burner configuration allows stabilization of the flame on the central tube under conditions, which otherwise prohibit stabilization of a single-stage flame (very fuel lean, very fuel rich and high gas velocity conditions) [13,16,17]. On the other hand, the secondary flame is not flat, which makes the comparison of the results with computer modeling simulations more difficult.

A small amount of iron pentacarbonyl vapors is added to this secondary flame as a precursor for iron oxide NP synthesis. The whole burner is mounted such that the gases propagate from top to bottom along the x coordinate (see Fig. 1). The burner is translated along this axis with the aid of stepper motor (Huntington Labs, model I-2252-8 controlled by Thorlabs controller BSC101, 0.1 mm accuracy), thus varying the distance from the burner (DFB) to the sampling orifice of the combined PMS-QCM apparatus. Thus, at DFB = 22 mm the sampler is located in the zone of the front of the secondary flame. The parameters of the flames used in this work are summarized in Table 1. The total pressure in the chamber is controlled to be 30 Torr by a feedback valve controller (model 252/253 MKS Instruments) with an exhaust throttle valve. The gas flows are controlled by mass flow controllers (MFC) (MKS Instruments). Vapors of the liquid IPC ( $\sim$ 8 Torr) are premixed in a 10 liter stainless steel vessel with nitrogen gas to a total pressure of 700-800 Torr. This mixture is added through an MFC to the secondary flame gases.

Samples were also collected over a carbon mesh copper grids, which were later analyzed under a high resolution transmission electron microscope (HRTEM, FEI Technai F20 TEM) to extract information concerning particle morphology, size distribution and crystal structure. During the sampling procedure the grids were placed into the particle-laden molecular beam in the sampling chamber through a special vacuum dock for times of 15 s–1 min.

#### 2.1. Particle mass spectrometer (PMS)

Below we elaborate in detail on the design and operation principle of the particle mass spectrometry used in this work. The detailed description provided below is a review of previous studies Download English Version:

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